Sensing the environment of V^{4+} dopant ions in a metal organic framework with EPR spectroscopy and X-ray diffraction

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MIL-53(Al) is a metal-organic framework (MOF) in which infinite chains of hydroxyl-sharing $AlO_4(OH)_2$ polyhedra are connected by benzene-dicarboxylate linkers, to form a three dimensional network with channel-like pores [1]. After liquid solution synthesis the pores are blocked by unreacted linker and solvent molecules. These can be removed either by calcination or by chemical solvent extraction. The resulting activated MOF structure exhibits breathing: depending on external conditions of temperature, pressure or the presence of certain guest molecules it changes from an open large pore (LP) to a contracted narrow pore (NP) state or vice versa. The as-synthesized, LP and NP states of this MOF can be clearly distinguished by powder X-ray diffraction (PXRD).

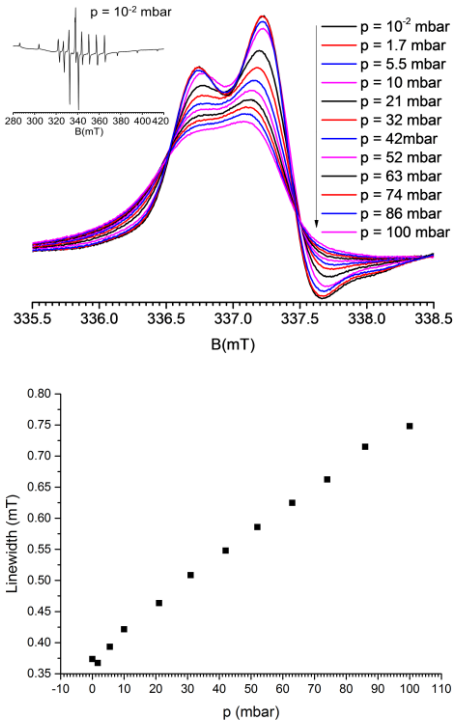

Figure 1. Oxygen pressure dependence of the EPR spectrum of V-doped MIL-53(Al) in the LP state. (top) EPR spectra, (bottom) linewidth vs. pressure.

When substituting a small fraction (up to a few percent) of the metal ions in MIL-53(Al) by vanadium, the breathing behaviour of this MOF is not altered. Part of these V-ions adopt the paramagnetic V^{4+} state ($3d^1$ electron configuration). The EPR spectrum of these dopant ions also allows to monitor transitions between NP and LP states of the MOF [2]. In this contribution, we show that the PXRD pattern is very sensitive to ambient humidity, while the EPR spectrum allows to detect O_2 down to pressures of the order of a few mbar.

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[1] T. Loiseau et al., *Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration*, Chem. - Eur. J., **2004**, 10, 1373−1382.

[2] I. Nevjestić et al., *In Situ Electron Paramagnetic Resonance and X ‑ray DiffractionMonitoring of Temperature-Induced Breathing and Related Structural Transformations in Activated V ‑Doped MIL-53(Al)*, J. Phys. Chem. C, **2016**, 120, 17400-17407.